

CLAIMS

1. A method of depositing a material onto a substrate, the method comprising the steps of:
- 5 (a) feeding a material solution comprising one or more precursor compounds, a solvent and a pH-modifying catalyst to an outlet to provide a stream of droplets of the material solution,
- 10 (b) generating an electric field to electrostatically attract the droplets from the outlet towards the substrate; and
- 15 (c) providing an increase in temperature between the outlet and the substrate.
2. A method according to claim 1, in which step (b) comprises:
- 15 applying a voltage to the outlet such that droplets of the material solution emerging from the outlet are charged and attracted to the substrate by virtue of the electric field.
3. A method according to claim 1 or claim 2, comprising the step of relatively rotating and/or translating the outlet and the substrate during coating deposition.
- 20 4. A method according to any one of the preceding claims, comprising the step of varying the material solution composition and/or concentration during the coating process.
- 25 5. A method according to any one of the preceding claims, comprising the step of reversing the polarity of the electric field between the outlet and the substrate at intervals during the deposition process.
- 30 6. A method according to any one of the preceding claims, comprising the step of locally heating areas of the substrate to enhance material deposition at the heated areas.

7. A method according to any one of the preceding claims, comprising the step of electrostatically and/or magnetically steering the stream of droplets in transit from the outlet to the substrate.
- 5 8. A method according to any one of the preceding claims, wherein the material is deposited as a film.
9. A method according to claim 8, wherein the film is a multicomponent oxide film; a simple oxide film or a doped film.
- 10 10. A method according to claim 8 or claim 9, wherein the film is one or more of: a structural film; a functional film; and an electroceramic film.
- 15 11. A method according to any one of claims 1 to 7, in which the material is deposited as a powder.
12. A method according to any one of the preceding claim, in which the material solution is a polymer solution.
- 20 13. A method according to claim 12, comprising the step of maintaining the applied electric field for at least part of the time during which the material deposited on the substrate is allowed to cool.
- 25 14. A method according to any one of the preceding claims, wherein the catalyst is an acid, added in sufficient quantity to give a material solution pH of between 2 and 5.
15. A method according to claim 14 wherein the catalyst is selected from the group consisting of: ethanoic acid and hydrochloric acid.
- 30 16. A method according to any one of claims 1 to 13, wherein the catalyst is an alkali, added in sufficient quantity to give a material solution pH of between 9 and 12.

17. A method according to claim 16 wherein the catalyst is NH₃.
18. A method according to any one of the preceding claims, wherein the droplets of material solution are charged to approximately 5-30 kilovolts with respect to the substrate.
19. A method according to any one of the preceding claims, wherein the temperature increases to a temperature in the approximate range from about 100 to about 650 degrees celsius.
20. A method according to any one of claims 1 to 18, wherein the temperature increases to a temperature in the approximate range from about 100 to about 400 degrees celsius.
- 15 21. A method according to any one of the preceding claims, wherein the method is performed within the confines of a container and the other ambient gaseous reactants are supplied to the container, thereby to enable the deposition of a particular film.
- 20 22. A method according to any one of claims 1 to 11, wherein the material is Lead Zirconate Titanate (PZT), and the material solution is manufactured by the steps of:
(a) mixing CH₃OCH₂CH₂OH (solvent) with a first precursor compound Pb(CH₃CO₂)₂ and Zr(OC₃H₇)₄ and a second precursor compound Ti(OC₃H₇)₄, and
25 (b) adding a catalyst to the mixture to provide a material solution of a required pH.
23. A method according to any one of claims 1 to 11, wherein the material is PbTiO₃, and the material solution is manufactured by the steps of:
(a) mixing CH₃OCH₂CH₂OH (solvent) with a first precursor compound Pb(CH₃CO₂)₂ and a second precursor compound Ti(OC₃H₇)₄, and
30 (b) adding a catalyst to the mixture to provide a material solution of a

required pH.

24. A method according to any one of claims 1 to 11, wherein the material is BaTiO₃, and the material solution is manufactured by the steps of:
- 5 (a) mixing CH₃OCH₂CH₂OH (solvent) with a first precursor compound Ba(CH₃CO₂)₂ and a second precursor compound Ti(OC₃H₇)₄, and
 (b) adding a catalyst to the mixture to provide a material solution of a required pH.
- 10 25. A method according to any one of claims 1 to 11, wherein the material is SnO₂-In₂O₃, and the material solution is manufactured by the steps of:
 (a) mixing ethanol (solvent) with a first precursor compound In(NO₃)₃.xH₂O and a second precursor compound SnCl₂, and
 (b) adding a catalyst to the mixture to provide a material solution of a required pH.
- 15 26. A method according to any one of claims 1 to 11, wherein the material is La(Sr)MnO₃, and the material solution is manufactured by the steps of:
 (a) mixing about 20% H₂O and about 80% ethanol (solvent) with a first precursor compound La(NO₃)₃.xH₂O and Mn(NO₃).6H₂O and a second precursor compound SrNO₃, and
 (b) adding a catalyst to the mixture to provide a material solution of a required pH.
- 20 27. A method according to any one of claims 1 to 11, wherein the material is Yttria Stabilised Zirconia (YSZ), and the material solution is manufactured by the steps of:
 (a) mixing propanol or butanol (solvent) with a first precursor compound Y(O₂C₈H₁₅)₃ and a second precursor compound Zr(OC₄H₉)₄, and
 (b) adding a catalyst to the mixture to provide a material solution of a required pH.
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28. A method according to any one of claims 1 to 11, wherein the material is Yttria Stabilised Zirconia (YSZ), and the material solution is manufactured by the steps of:

- (a) mixing propanol or butanol (solvent) with a first precursor compound $\text{Y}(\text{O}_2\text{C}_3\text{H}_{15})_3$ and a second precursor compound $\text{Zr}(\text{OC}_3\text{H}_7)_4$, and
- (b) adding a catalyst to the mixture to provide a material solution of a required pH.

29. A method according to any one of claims 1 to 11, wherein the material is NiO-YSZ, and the material solution is manufactured by the steps of:

- (a) mixing propanol (solvent) with a first precursor compound $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Zr}(\text{OC}_3\text{H}_7)_4$ and a second precursor compound $\text{Y}(\text{O}_2\text{C}_8\text{H}_{15})_3$, and
- (b) adding a catalyst to the mixture to provide a material solution of a required pH.

30. A method according to any one of the preceding claims, wherein the film has a thickness between a nanometre and approximately 100 micrometers.

31. Apparatus for depositing films on a substrate, the apparatus comprising:

- (a) an outlet for providing a stream of material solution droplets, the material solution comprising one or more precursor compounds, a solvent and a pH-modifying catalyst;
- (b) means for generating an electric field to electrostatically attract the droplets from the outlet towards the substrate; and
- (c) a heater for heating the substrate and providing an increase in temperature between the outlet and the substrate.

32. Apparatus according to claim 31, comprising a syringe pump to provide a stream of material solution to the outlet.

33. Apparatus according to claim 31 or 32, comprising a container for enclosing

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at least the substrate and the outlet, such that other gaseous reactants may be supplied for reaction with the material solution.

34. Apparatus according to any one of claims 31 to 33, comprising a heatable member disposed, at least in part, in a region between the substrate and the outlet, to provide, when heated, a temperature gradient between the outlet and the substrate.

35. Apparatus according to any one of claims 31 to 34, comprising one or more electrostatic and/or magnetic deflectors for deflecting the path of the droplets between the outlet and the substrate.

36. A method of depositing a material onto a substrate, the method comprising the steps of:

- (a) feeding a material solution to an outlet to provide a stream of droplets of the material solution,
- (b) generating an electric field to electrostatically attract the droplets from the outlet towards the substrate; and
- (c) providing an increase in temperature between the outlet and the substrate.